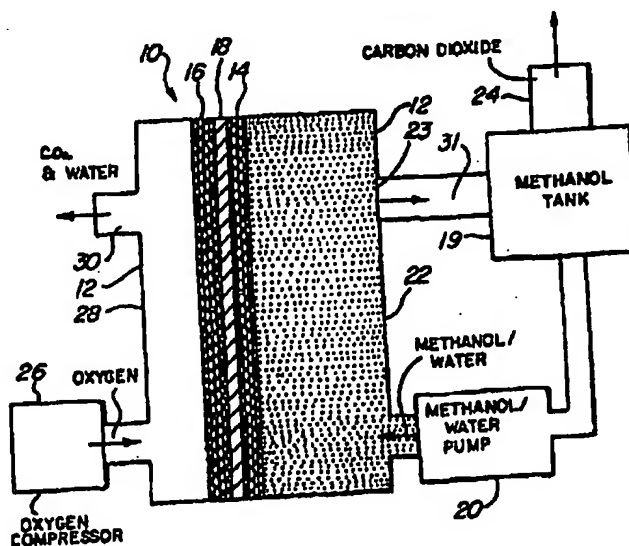


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(54) Title: ORGANIC FUEL CELL, AND METHODS OF OPERATION THEREOF AND MANUFACTURE OF ELECTRODE THEREFOR			



## (57) Abstract

A liquid organic fuel cell (10) is provided which employs a solid electrolyte membrane (18). An organic fuel, such as methanol/water mixture, is circulated past an anode (14) of the cell while oxygen or air is circulated past a cathode (16). The cell electrolyte membrane is preferably made of Nafion™. Also, a method for improving the performance of carbon electrode structures is provided, wherein a high-surface-area carbon particle/Teflon™ binder structure is immersed within a Nafion™/methanol bath to impregnate the electrode with Nafion™. A method of fabricating an anode for this fuel cell is described, wherein metal alloys are deposited onto the electrode from a solution containing perfluorooctanesulfonic acid. A fuel additive containing this acid, and new organic fuels are also described.

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ORGANIC FUEL CELL, AND METHODS OF OPERATION THEREOF AND  
MANUFACTURE OF ELECTRODE THEREFOR.

BACKGROUND OF THE INVENTION

Origin of the Invention:

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public LAW 96-517 (35 USC 202) in which the Contractor has elected to retain title.

Technical Field:

The invention generally relates to organic fuel cells and in particular liquid feed organic fuel cells.

Background Art:

Fuel cells are electrochemical cells in which a free energy change resulting from a fuel oxidation reaction is converted into electrical energy. In an organic/air fuel cell, an organic fuel such as methanol, formaldehyde, or formic acid is oxidized to carbon dioxide at an anode, while air or oxygen is reduced to water at a cathode. Fuel cells employing organic fuels are extremely attractive for both stationary and portable applications, in part, because of the high specific energy of the organic fuels, e.g., the specific energy of methanol is 6232 Wh/kg.

Two types of organic/air fuel cells are generally known:

1. An "indirect" or "reformer" fuel cell in which the organic fuel is catalytically reformed and processed into carbon monoxide-free hydrogen, with the hydrogen so obtained oxidized at the anode of the fuel cell.
2. A "direct oxidation" fuel cell in which the organic fuel is directly fed into the fuel cell without any

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previous chemical modification where the fuel is oxidized at the anode.

Direct oxidation fuel cells do not require a fuel processing stage. Hence, direct oxidation fuel cells offer a considerable weight and volume advantage over the indirect fuel cells. Direct oxidation fuel cells use either a vapor or a liquid feed of the organic fuel. Current art direct oxidation fuel cells that have shown promise typically employ a liquid feed design in which a liquid mixture of the organic fuel and a sulfuric acid electrolyte is circulated past the anode of the fuel cell.

The use of sulfuric acid electrolyte in the current-art direct methanol fuel cells presents several problems. The use of sulfuric acid, which is highly corrosive, places significant constraints on the materials of construction of the fuel cell. Typically, expensive corrosion resistant materials are required. Sulfate anions, created within the fuel cell, have a strong tendency to adsorb on the electrocatalyst, thereby hindering the kinetics of electro-oxidation of the fuel and resulting in poor performance of the fuel electrode. Also, sulfuric acid tends to degrade at temperatures greater than 80°C and the products of degradation usually contain sulfur which can poison the electrocatalyst. In multi-cell stacks, the use of sulfuric acid electrolyte can result in parasitic shunt currents.

Exemplary fuel cells of both the direct and indirect types are described in U.S. Patent Nos.: 3,013,908; 3,113,049; 4,262,063; 4,407,905; 4,390,603; 4,612,261; 4,478,917; 4,537,840; 4,562,123; and 4,629,664.

U.S. Patents 3,013,908 and 3,113,049, for example, describe liquid feed direct methanol fuel cells using a sulfuric acid electrolyte. U.S. Patents 4,262,063,

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4,390,603, 4,478,917 and 4,629,664 describe improvements to sulfuric acid-based methanol fuel cells wherein a high molecular weight electrolyte or a solid proton conducting membrane is interposed between the cathode and the anode as an ionically conducting layer to reduce crossover of the organic fuel from the anode to the cathode. Although the use of the ionically conducting layer helps reduce crossover, the ionically conducting layer is used only in conjunction with a sulfuric acid electrolyte. Hence, the fuel cell suffers from the various aforementioned disadvantages of using sulfuric acid as an electrolyte.

In view of the aforementioned problems associated with using sulfuric acid as an electrolyte, it would be desirable to provide a liquid feed fuel cell that does not require sulfuric acid as an electrolyte.

In addition to the improvements in operational characteristics of the liquid feed fuel cell, the conventional method of fabricating high-surface-area electro-catalytic electrodes for use such fuel cells also needs to be improved. The existing method of fabrication of fuel cell electrodes is a fairly time-consuming and expensive procedure. Specifically, electrode fabrication requires that a high surface-area carbon-supported alloy powder be initially prepared by a chemical method which usually requires about 24 hours. Once prepared, the carbon-supported alloy powder is combined with a Teflon™ binder and applied to a carbon fiber-based support to yield a gas diffusion electrode. To volatilize impurities arising out of the Teflon™ binder and to obtain a fibrous matrix of Teflon™, the electrodes are heated to 200-300°C. During this heating step, oxidation and sintering of the electrocatalyst can occur, resulting in a reduced activity of the surface of the electrode. Thus, the electrodes often require re-activation before use.

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Also electrodes produced by conventional methods are usually of the gas-diffusion type and cannot be effectively used in liquid feed type fuel cells as the electrode is not adequately wetted by the liquid fuel. In general, the structure and properties of a fuel oxidation electrode (anode) for use in liquid feed type fuel cells are quite different from the gas/vapor feed fuel cells such as the hydrogen/oxygen fuel cell. The electrode structures for use in a liquid feed fuel cell should be very porous and the liquid fuel solution should wet all pores. Carbon dioxide that is evolved at the fuel electrode should be effectively released from the zone of reaction. Adequate wetting of the electrodes is a major problem for liquid feed fuel cells--even for those which use a sulfuric acid electrolyte.

As can be appreciated, it would be desirable to provide improved methods for fabricating electrodes, particularly for use in liquid feed fuel cells. It is also desirable to devise methods for modifying electrodes, originally adapted for gas-feed fuel cells, for use in liquid feed fuel cells.

In addition to improving the liquid feed fuel cell itself and for providing improved methods for fabricating the electrodes of fuel cell, it would be desirable to provide new effective fuels as well. In general, it is desirable to provide liquid fuels which undergo clean and efficient electro-chemical oxidation within the fuel cell. The efficient utilization of organic fuels in direct oxidation fuel cells is, in general, governed by the ease by which the organic compounds are anodically oxidized within the fuel cell. Conventional organic fuels, such as methanol, present considerable difficulties with respect to electro-oxidation. In particular, the electro-oxidation of organic compounds such as methanol involves multiple electron transfer and is a very hindered process with

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several intermediate steps. These steps involve dissociative adsorption of the fuel molecule to form active surface species which undergo relatively facile oxidation. The ease of dissociative adsorption and surface reaction usually determines the facility of electro-oxidation. Other conventional fuels, such as formaldehyde, are more easily oxidized, but have other disadvantages as well. For example, formaldehyde is highly toxic. Also, formaldehyde is extremely soluble in water and therefore crosses over to the cathode of the fuel cell, thus reducing the performance of the fuel cell. Other conventional organic fuels, such as formic acid, are corrosive. Furthermore, many of the conventional organic fuels poison the electrodes of the fuel cell during electro-oxidation, thus preventing sustained operation. As can be appreciated, it would be desirable to provide improved fuels, particularly for use in liquid feed fuel cells, which overcome the disadvantages of conventional organic fuels, such as methanol, formaldehyde, and formic acid.

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## SUMMARY OF THE INVENTION

A general object of the invention is to provide an improved direct type liquid feed fuel cell. One particular object of the invention is to provide a direct type liquid feed fuel cell which does not require a sulfuric acid electrolyte. Another particular object of the invention is to achieve adequate wetting of electrodes for use in liquid feed fuel cells. Yet another particular object of the invention is to provide an improved method for wetting electrodes for use in fuel cells having sulfuric acid electrolytes. Still another particular object of the invention is to provide improved fuels for use in liquid feed fuel cells.

The object of providing an improved liquid feed direct fuel cell which does not require a sulfuric acid electrolyte is achieved in part by using a solid polymer electrolyte membrane in combination with a battery-type anode that is porous and is capable of wetting the fuel. In the improved liquid feed fuel cell, a battery-type anode structure and a cathode are bonded to either side of the solid polymer proton-conducting membrane forming a membrane-electrode assembly. A solution of methanol and water which is substantially free of sulfuric acid is circulated past the anode side of the assembly.

A solid polymer membrane is used, in part, because such membranes have excellent electrochemical and mechanical stability, high ionic conductivity, and can function both as an electrolyte and as a separator. Also, the kinetics of electro-oxidation of methanol and electro-reduction of air or oxygen are more facile at an electrode/membrane-electrolyte interface as compared to an electrode/sulfuric acid interface. The use of the membrane permits operation



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of the fuel cell at temperatures as high as 120°C. Since the fuel and water solution is substantially free of sulfuric acid, there is no need for expensive corrosion-resistant components in the fuel cell and its accessories. Also the absence of conducting ions in the fuel and water solutions, which can exist when a sulfuric acid electrolyte is employed, substantially eliminates the possibility of any parasitic shunt currents in a multi-cell stack.

The solid polymer electrolyte is preferably a proton-conducting cation-exchange membrane, such as the perfluorinated sulfonic acid polymer membrane, Nafion™. Nafion™ is a co-polymer of tetrafluoroethylene and perfluorovinylether sulfonic acid. Membranes of modified perfluorinated sulfonic acid polymer, polyhydrocarbon sulfonic acid and composites of two or more kinds of proton exchange membranes can also be used.

The anode is preferably formed from high surface area particles of platinum-based alloys of noble and non-noble metals. Binary and ternary compositions can be used for the electro-oxidation of organic fuels. Platinum-ruthenium alloy, with compositions varying from 10 - 90 atom percent of platinum, is the preferred anode electrocatalyst for the electro-oxidation of methanol. The alloy particles are either in the form of fine metal powders, i.e., "unsupported", or are supported on high surface area carbon material.

Conventional fuel cell anode structures (gas diffusion type) are not suitable for use in liquid feed type organic/air fuel cells. These conventional electrodes have poor fuel wetting properties. These conventional electrodes can be modified for use in liquid feed type fuel cells by coating them with substances that improve their wetting properties. Nafion™ with an equivalent weight of 1000 or

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higher is the preferred substance. The additive decreases interfacial tension of the liquid/catalyst interface and leads to the uniform wetting of the electrode pores and particles by the fuel and water solution, yielding enhanced utilization of the electrocatalyst. In addition to improving wetting properties, Nafion™ additive also provides ionic continuity with the solid electrolyte membrane and permits efficient transport of protons or hydronium ions generated by the fuel oxidation reaction. Further, the additive facilitates the release of carbon dioxide from the pores of the electrode. By using a perfluorinated sulfonic acid as the additive, anionic groups are not strongly adsorbed on the electrode/electrolyte interface. Consequently, the kinetics of electro-oxidation of methanol are more facile than in sulfuric acid electrolyte. Other hydrophilic proton-conducting additives with the desired properties include montmorillonite clay, alkoxycelluloses, cyclodextrins, mixtures of zeolites, and zirconium hydrogen phosphate.

The object of improving electrodes for operating in liquid feed fuel cells is achieved, in part, by using perfluorooctanesulfonic acid as an additive in an electro-deposition bath used in fabricating the electrode. An electro-deposition method using the perfluorooctanesulfonic acid additive comprises the steps of positioning a high-surface-area carbon electrode structure within a bath containing metallic salts, positioning an anode within the bath and applying a voltage between the anode and the cathode until a desired amount of metal becomes deposited onto the electrode. After deposition of the metal onto the electrode, the electrode is extracted from the bath and washed within deionized water.

Preferably, the metal salts include hydrogen hexachloroplatinate and potassium pentachloroauroruthenium. The

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anode is composed of platinum. The carbon electrode structure includes high-surface-area carbon particles bound together by polytetrafluoroethylene, sold under the trademark Teflon™.

The object of providing for adequate wetting of an electrode within a liquid feed fuel cell having a sulfuric acid electrolyte is achieved by employing perfluorooctanesulfonic acid as an additive to the fuel mixture of the fuel cell. Preferably, the perfluorooctanesulfonic acid is added to the organic fuel and water mixture in concentrations from 0.001 - 0.1 M.

The general objective of providing new fuels for use in organic fuel cells is achieved by using either trimethoxymethane, dimethoxymethane or trioxane. All three new fuels can be oxidized at a high rate into carbon dioxide and water within the fuel cell without poisoning the electrodes. Furthermore, neither trimethoxymethane, dimethoxymethane or trioxane are corrosive. Rates of oxidation of the three new fuels are comparable to, or better than, oxidation rates of conventional organic fuels. For example, rates of oxidation for dimethoxymethane are higher than that of methanol at the same temperature. Trioxane achieves oxidation rates comparable to that of formaldehyde. However, trioxane has a much higher molecular weight than formaldehyde and, as such, molecules of trioxane do not cross-over to the cathode of the fuel cell as easily as molecules of formaldehyde.

Trimethoxymethane, dimethoxymethane and trioxane may be employed in a fuel cell having any of the improvements set forth above. However, the improved fuels may also be advantageously used within other organic fuel cells, including entirely conventional fuel cells.

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Hence the various general objects of the invention set forth above are achieved. Other objects and advantages of the invention will be apparent from the detailed description set forth below.

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## BRIEF DESCRIPTION OF THE DRAWINGS

The objects and advantages of the present invention will become more readily apparent after reviewing the following detailed description and accompanying drawings, wherein:

Fig. 1 provides a schematic representation of an improved liquid feed organic fuel cell having a solid polymeric membrane configured in accordance with a preferred embodiment of the invention.

Fig. 2 provides a schematic representation of a multi-cell fuel system employing the improved liquid feed organic fuel cell of Fig. 1.

Fig. 3 is a graph illustrating the performance of a solid polymeric membrane electrolyte and a sulfuric acid electrolyte in liquid organic fuels.

Fig. 4 is a graph illustrating the performance of liquid feed fuel cell of Fig. 1 for methanol/air and methanol/oxygen combinations.

Fig. 5 is a graph illustrating the effect of fuel concentration on the performance of the liquid feed fuel cell of Fig. 1.

Fig. 6 is a graph illustrating the polarization behavior of the fuel electrode and cathode in the fuel cell of Fig. 1.

Fig. 7 is a block diagram illustrating a method for fabricating electrode containing hydrophilic proton-conducting ionomer additive for use in liquid feed cells.

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Fig. 8 is a graph illustrating the polarization characteristics for methanol oxidation at electrodes containing the ionomer additive and prepared in accordance with the procedure shown in Fig. 7.

Fig. 9 is a block diagram illustrating a method for fabricating an electrode employing perfluorooctanesulfonic acid within an electro-deposition bath.

Fig. 10 is a schematic illustration of an electrochemical cell for use in performing the method of Fig. 9.

Fig. 11 is a illustrating polarization curves for an electrode fabricating using the method of Fig. 9.

Fig. 12 is a graph illustrating polarization curves of a fuel cell using a sulfuric acid electrolyte and employing perfluorooctanesulfonic acid as a fuel additive.

Fig. 13 is a graph illustrating polarization curves of a fuel cell using dimethoxymethane as a fuel for various fuel concentration levels within a half cell having a sulfuric acid electrolyte.

Fig. 14 is a graph illustrating polarization curves of a fuel cell using dimethoxymethane as a fuel for differing temperatures and concentrations within a half cell having a sulfuric acid electrolyte.

Fig. 15 is a graph illustrating cell voltage as a function of current density for the fuel cell of Fig. 1 using dimethoxymethane as a fuel.

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Fig. 16 is a graph illustrating polarization curves of a fuel cell using trimethoxymethane as a fuel for various fuel concentration levels within a half cell having a sulfuric acid electrolyte.

Fig. 17 is a graph illustrating polarization curves of a fuel cell using trimethoxymethane as a fuel for differing temperatures and concentrations within a half cell having a sulfuric acid electrolyte.

Fig. 18 is a graph illustrating cell voltage as a function of current density for the fuel cell of Fig. 1 using trimethoxymethane or methanol as a fuel.

Fig. 19 is a graph illustrating polarization curves of a fuel cell using trioxane as a fuel for various fuel concentration levels within a half cell having a two molar sulfuric acid electrolyte.

Fig. 20 is a graph illustrating polarization curves of a fuel cell using trioxane as a fuel for differing temperatures and concentrations of sulfuric acid electrolyte within a half cell.

Fig. 21 is a graph illustrating cell voltage as a function of current density for the fuel cell of Fig. 1 using trioxane as a fuel.

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## DETAILED DESCRIPTION OF THE INVENTION

Referring to the figures, the preferred embodiments of the invention will now be described. Initially, an improved liquid feed organic fuel cell using a solid polymeric electrolyte membrane and a ionomeric anode additive is described, primarily with reference to Figs. 1 - 6. Then, a method for fabricating the anode having the ionomeric additive is described with reference to Figs. 7 - 8. A method for achieving improved wetting by fabricating an electrode within a bath containing perfluorooctanesulfonic acid is described with reference to Figs. 9 - 11. A fuel cell employing perfluorooctanesulfonic acid as a fuel additive is described with reference to Fig. 12. Fuel cells employing dimethoxymethane, trimethoxymethane and trioxane as fuels are described with reference to Figs. 13 - 21.

Fuel Cell Employing Solid Proton Conducting Electrolyte Membrane.

Fig. 1 illustrates a liquid feed organic fuel cell 10 having a housing 12, an anode 14, a cathode 16 and a solid polymer proton-conducting cation-exchange electrolyte membrane 18. As will be described in more detail below, anode 14, cathode 16 and solid polymer electrolyte membrane 18 are preferably a single multi-layer composite structure, referred to herein as a membrane-electrode assembly. A pump 20 is provided for pumping an organic fuel and water solution into an anode chamber 22 of housing 12. The organic fuel and water mixture is withdrawn through an outlet port 23 and is re-circulated through a re-circulation system described below with reference to Fig. 2 which includes a methanol tank 19. Carbon dioxide formed in the anode compartment is vented through a port 24 within tank



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19. An oxygen or air compressor 26 is provided to feed oxygen or air into a cathode chamber 28 within housing 12. Fig. 2, described below, illustrates a fuel cell system incorporating a stack of individual fuel cells including the re-circulation system. The following detailed description of the fuel cell of Fig. 1 primarily focuses on the structure and function of anode 14, cathode 16 and membrane 18.

Prior to use, anode chamber 22 is filled with the organic fuel and water mixture and cathode chamber 28 is filled with air or oxygen. During operation, the organic fuel is circulated past anode 14 while oxygen or air is pumped into chamber 28 and circulated past cathode 16. When an electrical load (not shown) is connected between anode 14 and cathode 16, electro-oxidation of the organic fuel occurs at anode 14 and electro-reduction of oxygen occurs at cathode 16. The occurrence of different reactions at the anode and cathode gives rise to a voltage difference between the two electrodes. Electrons generated by electro-oxidation at anode 14 are conducted through the external load (not shown) and are ultimately captured at cathode 16. Hydrogen ions or protons generated at anode 14 are transported directly across membrane electrolyte 18 to cathode 16. Thus, a flow of current is sustained by a flow of ions through the cell and electrons through the external load.

As noted above, anode 14, cathode 16 and membrane 18 form a single composite layered structure. In a preferred implementation, membrane 18 is formed from Nafion™, a perfluorinated proton-exchange membrane material. Nafion™ is a co-polymer of tetrafluoroethylene and perfluorovinylether sulfonic acid. Other membrane materials can also be used. For example, membranes of modified perfluorinated sulfonic acid polymer, polyhydrocarbon

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sulfonic acid and composites of two or more kinds of proton exchange membranes can be used.

Anode 14 is formed from platinum-ruthenium alloy particles either as fine metal powders, i.e. "unsupported", or dispersed on high surface area carbon, i.e. "supported". The high surface area carbon may be a material such as Vulcan XC-72A, provided by Cabot Inc., USA. A carbon fiber sheet backing (not shown) is used to make electrical contact with the particles of the electrocatalyst. Commercially available Toray™ paper is used as the electrode backing sheet. A supported alloy electrocatalyst on a Toray™ paper backing is available from E-Tek, Inc., of Framingham, Massachusetts. Alternately, both unsupported and supported electrocatalysts may be prepared by chemical methods, combined with Teflon™ binder and spread on Toray™ paper backing to produce the anode. An efficient and time-saving method of fabrication of electro-catalytic electrodes is described in detail herein below.

Platinum-based alloys in which a second metal is either tin, iridium, osmium, or rhenium can be used instead of platinum-ruthenium. In general, the choice of the alloy depends on the fuel to be used in the fuel cell. Platinum-ruthenium is preferable for electro-oxidation of methanol. For platinum-ruthenium, the loading of the alloy particles in the electrocatalyst layer is preferably in the range of 0.5 - 4.0 mg/cm<sup>2</sup>. More efficient electro-oxidation is realized at higher loading levels, rather than lower loading levels.

Cathode 16 is a gas diffusion electrode in which platinum particles are bonded to one side of membrane 18. Cathode 16 is preferably formed from unsupported or supported platinum bonded to a side of membrane 18 opposite to anode 14. Unsupported platinum black (fuel cell grade)

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